

Statistical and Thermal Physics: Homework 6

Due: 11 February 2020

1 Expansion and Compressibility

The isobaric expansion coefficient of any system quantifies how the system expands as its temperature increases and is

$$\alpha := \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P.$$

The isothermal compressibility quantifies how the system expands as its pressure increases and is

$$\kappa_T := -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T.$$

a) Show that, *for any system*

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial P}{\partial T} \right)_V$$

and check this for an ideal gas.

These can be used to check how the pressure must increase when the temperature is raised and while the volume of an object is held constant since

$$dP = \left(\frac{\partial P}{\partial T} \right)_V dT$$

if V is constant.

- b) In a particular temperature and pressure range the compressibility of water is $4.52 \times 10^{-10} \text{ Pa}^{-1}$ and the expansion coefficient is $2.1 \times 10^{-4} \text{ K}^{-1}$. Determine by how much the pressure on the water must increase to increase its temperature by 10° C while the volume is kept constant.
- c) In a particular temperature and pressure range the compressibility of gold is $4.5 \times 10^{-12} \text{ Pa}^{-1}$ and the expansion coefficient is $0.42 \times 10^{-4} \text{ K}^{-1}$. Determine by how much the pressure on the gold must increase to increase its temperature by 10° C while the volume is kept constant.
- d) Explain why it is more difficult to raise the temperature of water and gold by the same amount at constant volume rather than to do so at constant pressure.

2 Speed of sound in a material

A detailed analysis of vibrations in a material give that the speed of sound in a material is

$$v_{\text{sound}} = \sqrt{\frac{\partial P}{\partial \rho}}$$

where P is the pressure of the material and ρ the mass per unit volume.

- a) Show that for sound in any gas

$$v_{\text{sound}} = \sqrt{\frac{B}{\rho}}$$

where the bulk modulus is

$$B = -V \frac{\partial P}{\partial V}$$

- b) Determine the bulk modulus for an ideal gas that undergoes an isothermal process and use the result to determine an expression for the speed of sound if the sound propagation occurs via an isothermal process.
- c) Show that for an adiabatic process

$$B = \gamma P$$

where $\gamma = c_P/c_V$. Use the result to determine an expression for the speed of sound if the sound propagation occurs via an adiabatic process.

- d) How do the two speeds compare? Which process is more likely to occur for sound propagation in air?
- e) Assume that air is an ideal gas determine a value for the speed of sound in air as predicted by the above analysis.

3 Enthalpy and specific heat

- a) Determine an expression for the enthalpy in terms of T , P , and V for a monoatomic ideal gas (this will require using the known expressions for internal energy). Use the expression for enthalpy to determine expressions for c_V and c_P .
- b) Determine an expression for the enthalpy in terms of T , P , and V for a diatomic ideal gas. Use this to determine expressions for c_V and c_P . *For a diatomic ideal gas $E = \frac{5}{2} PV$.*
- c) For carbon monoxide, measurements give that, provided that the temperatures are between 298.15 K and 1200 K, the enthalpy per mole is

$$H = H_0 + AT + \frac{B}{2} T^2 + \frac{C}{3} T^3$$

where $A = 25.57 \text{ J/mol K}$, $B = 6.096 \times 10^{-3} \text{ J/mol K}^2$, $C = 4.055 \times 10^{-6} \text{ J/mol K}^3$ and T is the temperature in Kelvin (source: NIST Chemistry webbook). Determine an expression for the heat capacity at constant pressure per mole for carbon monoxide. Determine the heat capacities at 300 K and 400 K? How do these compare to the heat capacity for a diatomic ideal gas?

- d) Suppose that 1 mol of this gas is kept at constant pressure. Determine the heat needed to raise the temperature from 300 K to 350 K. Determine the heat needed to raise the temperature from 350 K to 400 K.

e) *Optional (up to 5 points extra credit):* For any gas

$$c_P = \left(\frac{\partial H}{\partial T} \right)_P$$

allows one to determine one partial derivative of $H(T, P)$ from experimental measurements. By following a similar scheme as was done for energy, show how one can relate the other partial derivative

$$\left(\frac{\partial H}{\partial P} \right)_T$$

to c_V and c_P .

4 Fire syringe

A fire syringe consists of a cylinder containing a gas. The gas can be compressed rapidly - this process is adiabatic. Consider a cylinder that contains a diatomic ideal gas initially at 300 K (room temperature). Suppose that the initial volume of the cylinder is V_i and the final volume is V_f .

- Determine an expression for the ratio of temperatures T_f/T_i in terms of V_i and V_f .
- Choose a material that you would like to ignite and determine the compression ratio V_f/V_i so that a fire syringe will ignite the material. Supply any relevant data needed to answer the question.

5 Deflated footballs

In the 2014 AFC Championship game, footballs were apparently deflated. NFL regulations require that the pressure of the football be between 12.5 psi and 13.5 psi. It is possible that the footballs could have been deflated during play as a result of the temperature drop between room where they were inflated and the outside. Suppose that the balls were inflated to 13 psi in a room at 75° F and then taken outside where the temperature was 51° F. Assume that the air inside the ball was an ideal gas. Note that the stated pressures are gauge pressures, i.e. pressure above atmospheric pressure. Also the game was played in Boston, MA, which is at sea level.

- Suppose that the volume of the ball remained constant. Determine the pressure of the air inside the ball once it is in equilibrium outside. In this process is any work done on the ball? Does heat enter or leave the ball?
- Suppose that the ball were inflated from 0 psi to 13 psi. Assume that the air was initially at room temperature before it was pumped into the ball and that the pumping process was adiabatic. Determine the temperature of the ball (in the room) immediately after it had been pumped up. This ball is then taken outside. Determine the pressure in the ball once it reaches equilibrium outside.
- Would either of these explain a reduction in pressure to 11.5 psi?

$$a) \quad \frac{\alpha}{K_T} = \frac{1/V}{\left(\frac{\partial V}{\partial T}\right)_P} \left/ \frac{1}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} \right.$$

$$= - \left(\frac{\partial V}{\partial T}\right)_P / \left(\frac{\partial V}{\partial P}\right)_T$$

But $\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T = 1 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = 1 / \left(\frac{\partial V}{\partial P}\right)_T$

Thus $\frac{\alpha}{K_T} = - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$

Then $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = - \left(\frac{\partial P}{\partial T}\right)_V$ gives $\frac{\alpha}{K_T} = \left(\frac{\partial P}{\partial T}\right)_V$

ideal gas

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk}{VP} = \frac{1}{T}$$

$$K_T = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = + \frac{1}{V} \frac{NkT}{P^2} = \frac{1}{P}$$

$$\frac{\alpha}{K_T} = \frac{P}{T}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V} = \frac{PV/T}{V} = \frac{P}{T}$$

works ✓

b) We get $dP = \frac{\alpha}{K_T} dT$

Here $dT = 10K$ and $\frac{\alpha}{K_T} = \frac{2.1 \times 10^{-4} K^{-1}}{4.52 \times 10^{-10} Pa} = 4.6 \times 10^5 Pa K^{-1}$

so $dP = 4.6 \times 10^6 Pa = 46 atm$

Pressure must increase by 46 atm!

c) Here $dP = \frac{\alpha}{K_T} dT = \frac{0.42 \times 10^{-4} K^{-1}}{4.5 \times 10^{-9} Pa^{-1}} \times 10 K = 9.3 \times 10^4 Pa$

should have been 10^{-12}

$= 0.92 atm$ **920 atm**

d) Need large change in pressure to keep volume constant. So it is easier to let volume change and expose to atmosphere ($P = \text{const}$)

a) Need $\frac{\partial P}{\partial \rho}$

Here $P = P(V)$ but $V = V(\rho)$

$$\Rightarrow \frac{dP}{d\rho} = \frac{dP}{dV} \frac{dV}{d\rho}$$

Now $\rho = M/V$ where M is the mass of the gas. So $V = M/\rho$

gives:

$$\frac{dV}{d\rho} = -M/\rho^2$$

and $M = \rho V$ gives

$$\frac{dV}{d\rho} = -\frac{V}{\rho}$$

$$\text{Thus } \frac{dP}{d\rho} = -\frac{V}{\rho} \frac{dP}{dV} = \frac{B}{\rho} \Rightarrow V_S = \sqrt{\frac{B}{\rho}}$$

$$b) P = \frac{NkT}{V} \text{ and } T \text{ is constant} \Rightarrow B = -V \left(-\frac{NkT}{V^2} \right) = \frac{NkT}{V} = P$$

so $V_S = \sqrt{\frac{P}{\rho}}$
isothermal

$$c) \text{ Here } PV^\gamma = \alpha = \text{const} \Rightarrow P = \frac{\alpha}{V^\gamma} \Rightarrow \frac{dP}{dV} = -\gamma \frac{\alpha}{V^{\gamma+1}}$$

$$\text{But } \alpha = PV^\gamma \Rightarrow \frac{dP}{dV} = -\gamma \frac{PV^\gamma}{V^{\gamma+1}} = -\frac{\gamma P}{V}$$

$$\Rightarrow B = \gamma P$$

Thus

$$V_{s \text{ adiabatic}} = \sqrt{\gamma \frac{P}{\rho}} = \sqrt{\gamma} \sqrt{\frac{P}{\rho}} \Rightarrow V_{s \text{ adiab}} = \sqrt{\gamma} \sqrt{\frac{P}{\rho}}$$

d) So $V_{s \text{ adiab}} = \sqrt{\gamma} V_{s \text{ isotherm.}}$

larger than 1 $\Rightarrow V_{s \text{ adiab}} \geq V_{s \text{ isotherm.}}$

Adiabatic, the process will be too quick for heat to enter/leave.

e) $P = 1.01 \times 10^5 \text{ Pa}$ at sea level

$\rho = 1.23 \text{ kg/m}^3$

$\Rightarrow \sqrt{\frac{P}{\rho}} = 287 \text{ m/s}$

Then for a diatomic gas $\gamma = \frac{7}{5}$

$\Rightarrow V_{s \text{ adiab}} = \sqrt{\frac{7}{5}} \times 287 \text{ m/s} = 339 \text{ m/s}$

In general

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

and for C_V we use $H = E + PV \Rightarrow E = H - PV$

$$dE = dH - PdV - VdP$$

But $dE = \delta Q - PdV \Rightarrow \delta Q - PdV = dH - PdV - VdP$

$$\Rightarrow \delta Q = dH - VdP$$

This is the starting point for determining specific heats. For C_V we need the r.h.s in terms of dT and dV . Here

$$dH = \left(\frac{\partial H}{\partial T} \right)_V dT + \left(\frac{\partial H}{\partial V} \right)_T dV$$

$$dP = \left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV$$

$$\Rightarrow \delta Q = \underbrace{\left[\left(\frac{\partial H}{\partial T} \right)_V - V \left(\frac{\partial P}{\partial T} \right)_V \right]}_{C_V} dT + [\text{expression}] dV$$

Thus $C_V = \left(\frac{\partial H}{\partial T} \right)_V - V \left(\frac{\partial P}{\partial T} \right)_V$

For monoatomic gases $E = fNkT = fPV$

$$\Rightarrow H = E + PV = (f+1)PV$$

$$\Rightarrow H(T, P) = (f+1)NkT = H(T, V)$$

a) Here $f = \frac{3}{2} \Rightarrow H = \frac{5}{2} NkT$

$$\Rightarrow C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{5}{2} Nk$$

$$\Rightarrow C_V = \left(\frac{\partial H}{\partial T} \right)_V - V \left(\frac{\partial P}{\partial T} \right)_V = \frac{5}{2} Nk - V \left(\frac{Nk}{V} \right) \quad \text{using } P = \frac{NkT}{V}$$

$$\Rightarrow C_V = \frac{3}{2} Nk$$

b) Here $f = \frac{5}{2}$ and $H = \frac{7}{2} NkT$

$$\left. \begin{array}{l} C_P = \frac{7}{2} Nk \\ C_V = \frac{5}{2} Nk \end{array} \right\} \text{ by same analysis as } \nearrow$$

c) $C_P = \left(\frac{\partial H}{\partial T} \right)_P$

$$= A + BT + CT^2$$

At 300K

$$C_P = 25.57 \text{ J/mol K} + 6.096 \times 10^{-3} \frac{\text{J}}{\text{mol K}^2} 300\text{K}$$

$$+ 4.055 \times 10^{-6} \frac{\text{J}}{\text{mol K}^2} \times 300\text{K}^2$$

$$= 25.57 \text{ J/mol K} + 1.83 \text{ J/mol K} + 0.36 \text{ J/mol K} = 27.76 \text{ J/mol K}$$

At 400K

$$C_P = \dots = 28.66 \text{ J/mol K}$$

We expect $\frac{5}{2} Nk$ for N particles. So for 1 mol $N = N_A$

$$\Rightarrow C_P = \frac{7}{2} \times 6.022 \times 10^{23} \times 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} = 29.09 \text{ J/mol K}$$

d) $dE = \delta Q - PdV$

$$E = H - PV \Rightarrow dE = dH - PdV - VdP$$

$$\Rightarrow dH - \cancel{PdV} - VdP = \delta Q - \cancel{PdV}$$

If pressure is constant $\delta Q = dH$

$$\Rightarrow Q = \Delta H$$

In both cases

$$\Delta H = H_0 + AT_f + \frac{B}{2} T_f^2 + \frac{C}{3} T_f^3$$

$$- (H_0 + AT_i + \frac{B}{2} T_i^2 + \frac{C}{3} T_i^3)$$

$$\Delta H = A \Delta T + \frac{B}{2} (T_f^2 - T_i^2) + \frac{C}{3} (T_f^3 - T_i^3)$$

From 300K \rightarrow 350K

$$\Delta H = A 50K + \frac{B}{2} ((350K)^2 - (300K)^2) + \frac{C}{3} [(350K)^3 - (300K)^3] \text{ per mol}$$

$$= 1280J + 99J + 21J = 1400J \Rightarrow Q = 1400J$$

From 350K - 400K

$$\Delta H = 1280J + 114J + 28.5J \Rightarrow Q = 1422J$$

e)

$$\delta Q = dH - V dP$$

$$= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP - V dP$$

$$= \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP$$

$$\hookrightarrow = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$= \left\{ \left(\frac{\partial H}{\partial T}\right)_P + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \left(\frac{\partial P}{\partial T}\right)_V \right\} dT + \{ \dots \} dV$$

Thus

$$C_V = \underbrace{\left(\frac{\partial H}{\partial T}\right)_P}_{C_P} + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow C_P - C_V = \left(\frac{\partial P}{\partial T}\right)_V \left[V + \left(\frac{\partial H}{\partial P}\right)_T \right]$$

$$\Rightarrow \frac{C_P - C_V}{\left(\frac{\partial P}{\partial T}\right)_V} - V = \left(\frac{\partial H}{\partial P}\right)_T$$

a) For an adiabatic process

$$PV^\gamma = \text{const}$$

For an ideal gas

$$PV = NkT \Rightarrow P = \frac{NkT}{V}$$

Thus

$$\frac{NkT}{V} V^\gamma = \text{constant}$$

$$\Rightarrow TV^{\gamma-1} = \text{constant}$$

$$\text{So } T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \Rightarrow \frac{T_f}{T_i} = \left(\frac{V_i}{V_f} \right)^{\gamma-1}$$

b) Paper about 230°C , initially at room temperature $= 20^\circ\text{C}$

$$T_i = 293\text{K}$$

$$T_f = 503\text{K}$$

$$\text{So } \left(\frac{T_f}{T_i} \right) = \left(\frac{V_i}{V_f} \right)^{\gamma-1} \Rightarrow \frac{V_f}{V_i} = \left(\frac{T_i}{T_f} \right)^{1/\gamma-1}$$

$$\text{Here } \gamma = C_p/C_v = 7/2 / 5/2 = 7/5 \Rightarrow \gamma-1 = 2/5 \Rightarrow \frac{1}{\gamma-1} = 5/2$$

$$\text{Thus } \frac{V_f}{V_i} = \left(\frac{T_i}{T_f} \right)^{5/2} = \left(\frac{293\text{K}}{503\text{K}} \right)^{5/2} = \boxed{0.26}$$

There are a number of essential facts.

* pressures given are all gauge pressures and need to be converted

$$P = P_{\text{atm}} + P_{\text{gauge}}$$

The game was played at sea level so $P_{\text{atm}} = 1.01 \times 10^5 \text{ Pa}$.

Then the conversion from psi to Pa is:

$$1 \text{ psi} = 6894 \text{ Pa} \quad \text{or} \quad 1 \text{ Pa} = 1.45 \times 10^{-4} \text{ psi}$$

Thus

Gauge in psi	Gauge in Pa	P in Pa
13 psi	$8.96 \times 10^4 \text{ Pa}$	$1.91 \times 10^5 \text{ Pa}$
11.5 psi	$7.93 \times 10^4 \text{ Pa}$	$1.82 \times 10^5 \text{ Pa}$
0 psi	0 Pa	$1.01 \times 10^5 \text{ Pa}$

* temperatures are converted via:

$$T_C = [T_F - 32] \frac{5}{9} \quad T_K = T_C + 273$$

$$\Rightarrow T_K = [T_F - 32] \frac{5}{9} + 273$$

T_F	T_K
75	297 K
51	284 K.

a) $PV = NkT \Rightarrow P/T = \frac{Nk}{V}$ is constant

$$\frac{P_f}{T_f} = \frac{P_i}{T_i} \Rightarrow P_f = P_i \frac{T_f}{T_i}$$

Then the data gives $P_f = 1.91 \times 10^5 \text{ Pa} \left(\frac{284}{297} \right)$

$$P_f = 1.83 \times 10^5 \text{ Pa} \quad \checkmark$$

This is not as low as the indicated gauge pressure
 \Rightarrow does not explain.

Here volume is constant $\Rightarrow W = 0$ and $\Delta E = Q + W \Rightarrow \Delta E = Q$

But $\Delta E < 0$ (since T drops) $\Rightarrow Q < 0$ heat leaves

b) Two stages

① Adiabatic compression results in a higher intermediate temp

② Cool at constant volume lowers temp + pressure.

Initial		Intermediate		Final
$P_0 = 1.01 \times 10^5 \text{ Pa}$	<u>adiab</u>	$P_1 = 1.91 \times 10^5 \text{ Pa}$	<u>const</u>	$P_2 = ??$
$T_0 = 297 \text{ K}$	\rightarrow	$T_1 = ??$	<u>vol</u>	$T_2 = 284 \text{ K}$

In adiabatic $PV^\gamma = \text{const} \quad V = \frac{NkT}{P}$

$$\Rightarrow P^{1-\gamma} T^\gamma = \text{const}$$

$$\Rightarrow P_1^{1-\gamma} T_1^\gamma = P_0^{1-\gamma} T_0^\gamma \Rightarrow T_1 = T_0 \left(\frac{P_0}{P_1} \right)^{\frac{1-\gamma}{\gamma}}$$

Here $\gamma = \frac{7}{5}$

$$\Rightarrow \frac{1-\gamma}{\gamma} = -\frac{2/5}{7/5} = -\frac{2}{7}$$

Thus $T_1 = T_0 \left(\frac{P_0}{P_1} \right)^{-2/7}$

$$\Rightarrow T_1 = T_0 \left(\frac{P_1}{P_0} \right)^{2/7} = 297 \text{ K} \left(\frac{1.91}{1.01} \right)^{2/7}$$

$$\Rightarrow T_1 = 356 \text{ K}$$

Then in the second process

$$\begin{aligned} \frac{P_2}{P_1} &= \frac{T_2}{T_1} \quad \Rightarrow \quad P_2 = P_1 \frac{T_2}{T_1} \\ &= 1.91 \times 10^5 \text{ Pa} \frac{284 \text{ K}}{356 \text{ K}} \end{aligned}$$

$$P_2 = 1.5 \times 10^5 \text{ Pa}$$

This gives a gauge pressure of: 7.5 psi

c) Adiabatic could explain it.